Actinide Crystallization Process Application for LWR Spent Fuel Treatment

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Introduction

1) The present work grew out of previous efforts in Germany to reduce the cost of PUREX operations by replacing the solvent extraction cycles used for U and Pu purification with a crystallization process

2) Bench-scale work showed that hexavalent actinides can be selectively crystallized from nitric acid solution as $AnO_2(NO_3)_2 \cdot xH_2O$ complexes at low temperature and yields of about 95% were achievable (-20 to -40 C)

3) Two successive crystallizations of uranyl nitrate showed decontamination factors of 100-1000 from selected fission products

4) Work on the process stopped with the end of the German reprocessing program

Introduction

5) More recently, Japanese groups have begun looking at crystallization of uranyl nitrate from dissolved LWR fuel before the PUREX extraction process. This reduces the size and cost of the PUREX operation and is predicted to reduce the overall plant size and cost.
6) One proposed process would cool the nitric acid dissolver solution from 40 C to 10 C and recover about 60% of the uranium. The remaining uranium and plutonium would be co-extracted in the PUREX operation and fabricated into fuel for a fast breeder reactor.
7) Bench-scale work on a simulated dissolver solution with 13 fission products produced uranyl nitrate crystals with DFs of 10-100 after three washes.

Actinide Crystallization Process

Objective: Evaluate actinide crystallization processes to remove U and other actinides from nitric acid and carbonate solutions and estimate potential to reduce cost of LWR spent fuel processing relative to UREX

Project Team:

Nuclear Materials Technology Division

Actinide Process Chemistry

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Actinide and Fuel Cycle Technologies

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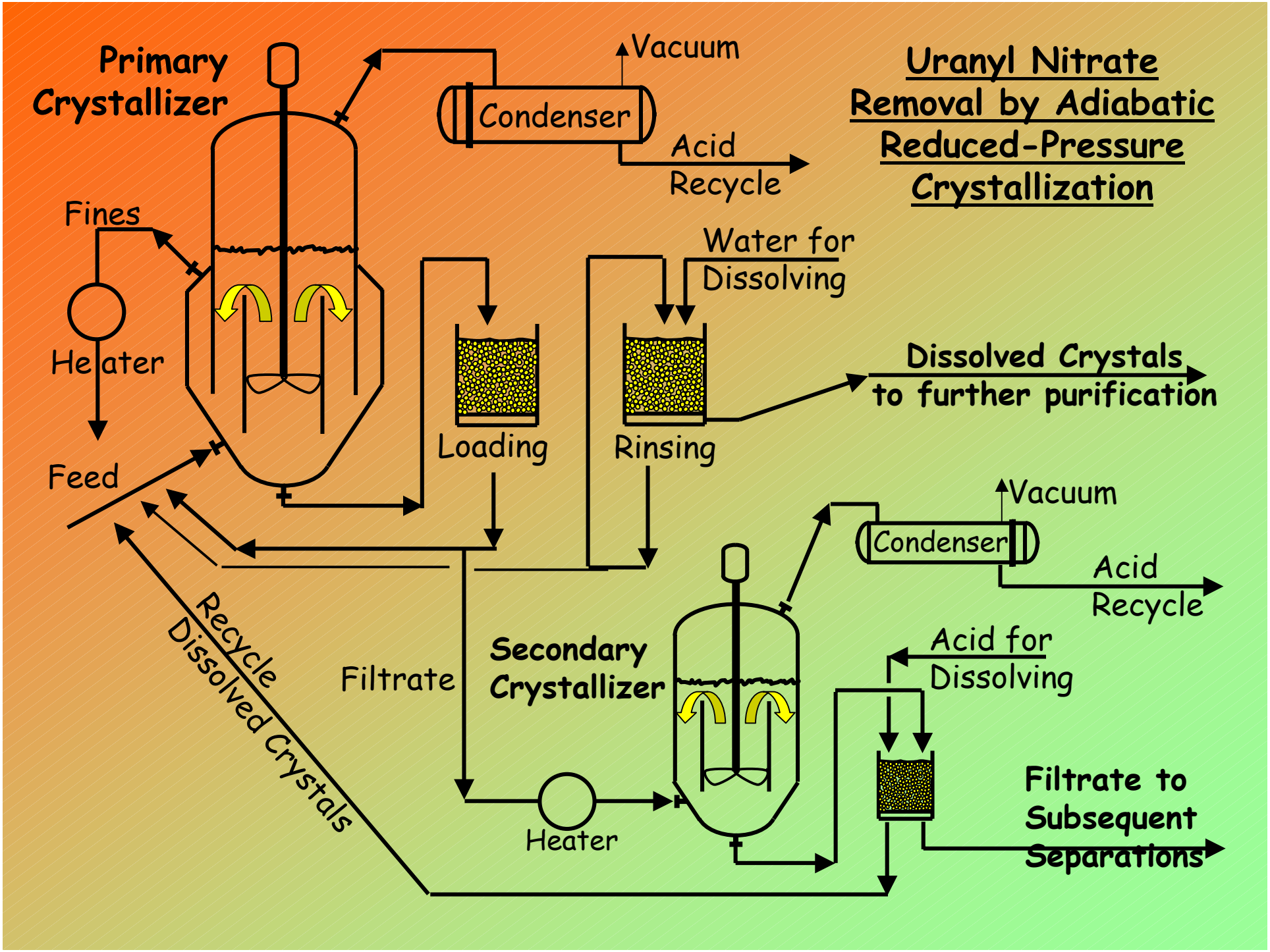
FY03 budget $900K

Actinide Crystallization Process

Nitric acid process overview:

- Dissolve spent fuel in nitric acid and filter/clarify to give concentrated solution of uranyl nitrate in 5-10 M HNO_3
- Crystallize uranyl nitrate complexes from nitric acid solution at low T (-20 to -40 C) or by evaporative concentration
- Use several stages of recrystallization-washing to obtain desired decontamination factor
- Uranium(VI) can be partitioned alone, leaving Pu and Np with fission products for subsequent aqueous or pyrochemical separations
- Pu(VI) and Np(VI) can be co-crystallized with U(VI) under oxidizing conditions and subsequently separated by changing oxidation state


Primary Crystallizer
Vacuum
Condenser
Acid Recycle
Uranyl Nitrate Removal by Adiabatic Reduced-Pressure Crystallization
Fines
Water for Dissolving
Heater
Dissolved Crystals to further purification
Loading
Rinsing
Feed
Vacuum
Condenser
Acid Recycle
Recycle Dissolved Crystals
Filtrate
Secondary Crystallizer
Acid for Dissolving
Heater
Filtrate to Subsequent Separations

Summary - Adiabatic Reduced-pressure Crystallizer Operation for U removal.

2000 metric tons/yr, 5000 hrs/yr operation, one of 4 parallel units.

	Dissolver Effluent		Condenser	Crystals	Filtrate
L/min	3.18		0.86	0.90	0.77
g/min	4929		1034	2778	1117
$UO_2(NO_3)_2$	2632	→ Flash Crystallizer P, mm-Hg	0	2180	452
Dissolved Salts	185		0	0	185
HNO_3	749		427	0	323
H_2O	1362	11.9	607	598	158
Temp, Deg.C	34.8		30	30	30

This is an adiabatic flash to cool & precipitate UNH crystals

83% Removal of UN

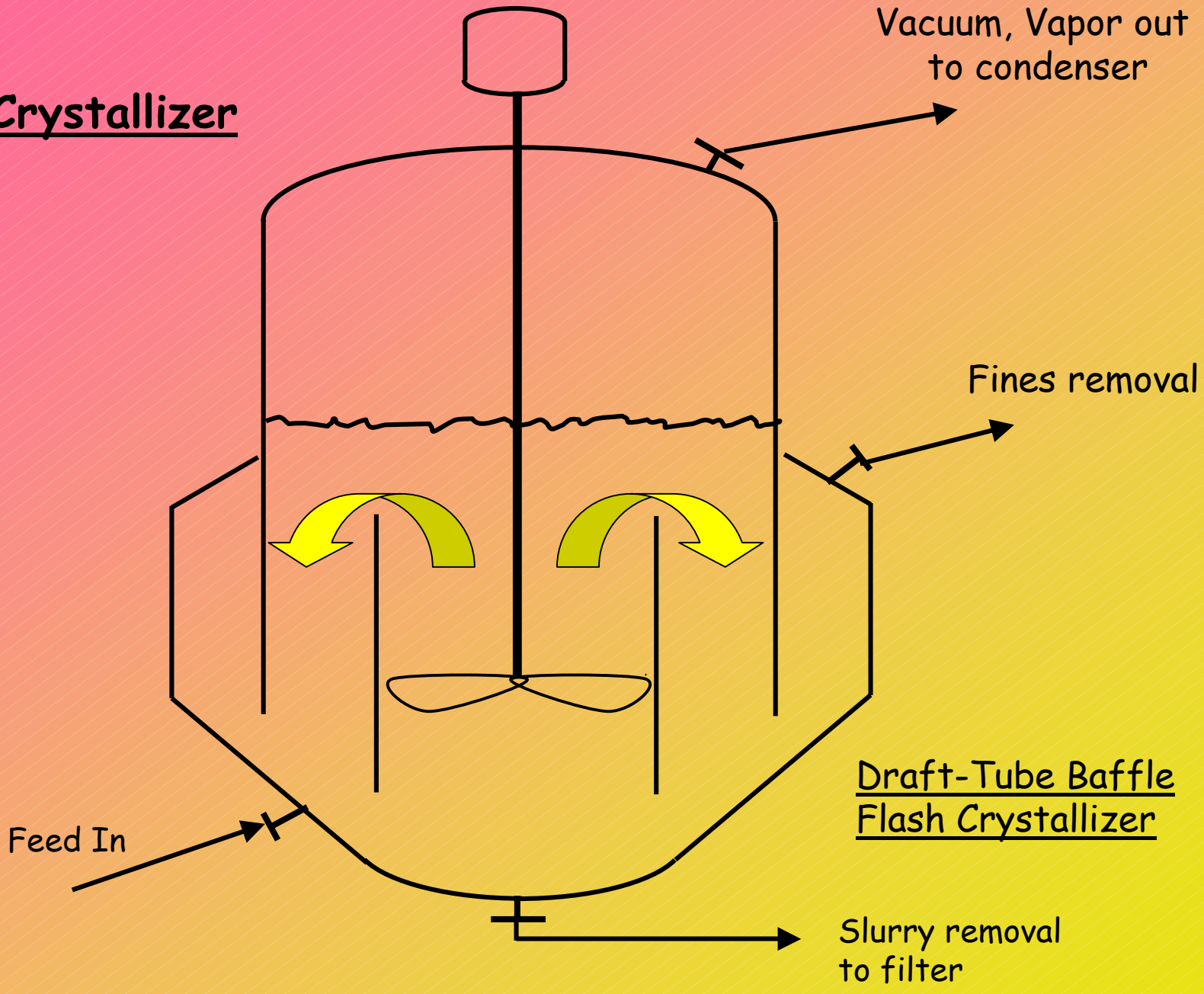
76% Volume Reduction.

Operates without heat input or any refrigerant.

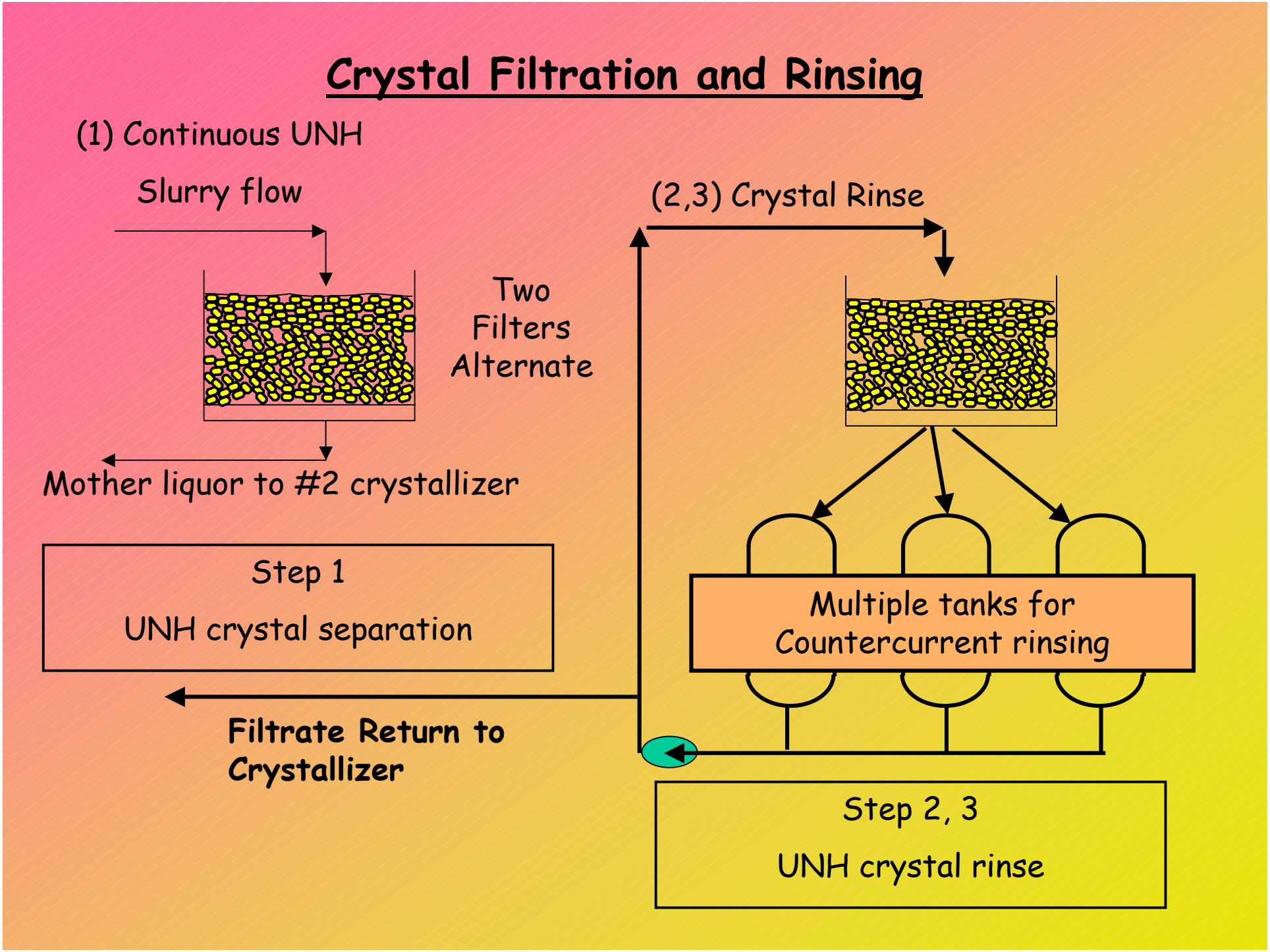
Requires mild vacuum operation and good controls.

Crystallizer size estimate: 90 min. residence time based on 2 liter/minute = 180 liters; ~21" Dia, 42" Hi.

UNH Crystallizer



Crystal Filtration and Rinsing



Actinide Crystallization Process Design Data

- Use bench-scale glassware to crystallize uranyl nitrate hydrates from simulant solutions containing selected fission product elements
- Decontamination factors of uranium from fission products will be measured by ICP-AES, ICP-MS or radiotracer methods
- Loop crystallizing apparatus will be operated to gain more detailed information on control of crystallization needed to design continuous unit

Actinide Crystallization Process - Carbonate Process

Uranium recovered on large scale from various ores using sodium carbonate dissolution and precipitation of sodium uranates

Process overview:

- Dissolve spent fuel in carbonate solution (cations have important influence on the solution chemistry, e.g., potassium, ammonium, sodium)
- Separate dissolved actinides and fission products from insoluble materials, e.g., Ba, Sr, Ln, insoluble fission products incorporated in waste package
- Adjust pH, carbonate-bicarbonate concentration, ammonium concentration, etc., to crystallize actinide complexes
- Uranium(VI) can be partitioned alone, leaving TRUs with fission products for subsequent separation steps (e.g., PYRO-A)
- TRU elements can be crystallized by adjusting conditions to form carbonate and/or hydroxide complexes
- Soluble fission products remain in solution for conversion to suitable waste form